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Test method

Tensile testing of individual glassy, rubbery and hydrogel electrospun polymer nanofibres to high strain using the atomic force microscope

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ABSTRACT

The production and use of polymer nanofibre assemblies prepared by electrospinning is now widespread. It is known that the tensile properties of electrospun polymer fibres can be different to those of bulk polymers. Here, we report a general method for measuring the tensile properties of individual electrospun nanofibres that employs a commercial atomic force microscope. Methods for preparing samples, force calibration and calculation of tensile stress and strain are described along with error estimation. By appropriate choice of AFM cantilever, it is shown that the tensile stress-strain curves can be measured for glassy, rubbery and gel polymer nanofibres. Testing can be in air or fluid and to strains of 300%. Example results illustrate the usefulness of the technique with the observation of high ductility in normally brittle glassy polymers such as polystyrene, and unusually large hysteresis in thermoplastic elastomer nanofibres. These observations provide new insights into the structure and mechanical behaviour of nanoscale polymeric materials.

1. Introduction

There is considerable interest in the production of polymers as nanofibres with applications ranging from bioengineering [1–6] such as wound dressings [7], tissue engineering scaffolds [8–11], and implantable drug delivery membranes [12] to energy applications such as high surface area electrodes in fuel cells [13], photovoltaics [14] or batteries [15,16] to water treatment applications as membranes [17,18] and functionalised filters [19,20]. In nearly all of these applications the mechanical properties of both the polymer nanofibres, and their assemblies, are important. The nanofibres require a minimum strength for handling and use, and in some cases, such as tissue engineering, the Young's modulus needs to be tailored to a specific range. The mechanical properties of the polymer nanofibre assemblies in the form of macro-scale mats are readily investigated using traditional testing methods [18,21–25]. However, mechanical tests on nanofibre assemblies are dominated by the strength of interfibre junctions, the radius of curvature of the fibres and the alignment of fibres, with the observed properties vastly different to the properties of individual fibres [26,27]. Appreciation of the mechanical properties of isolated electrospun polymer fibres is an emerging field.

A variety of methods have been developed for mechanical testing of individual polymer nanofibres [28] but, so far, no single 'best' approach has emerged. The existing methods range from the use of commercial universal testing machines [29–31], to microelectronic mechanical systems (MEMS) [32–35] and the use of atomic force microscope (AFM) cantilevers observed under either a

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scanning electron microscope (SEM) [36–39] or optical microscope [40,41], to a broad range of approaches relying on the AFM for all measurements.

The ideal testing method would be simple and rapid; provide reliable and accurate results; and be applicable to a wide range of materials tested in a variety of different environments. The best available universal testing machines have a minimum force resolution of 50 nN, which limits their use for testing individual nanofibres. MEMS force sensors are more accurate, but their use requires either *in situ* SEM [32,33] or the sensor needs to be glued to the fibre after mounting onto the MEMS testing platform [34,35]. These processes are cumbersome, creating a long downtime between samples, and have not been demonstrated for testing in liquid environments.

The AFM has been a popular tool for nano-mechanical measurements since these instruments incorporate both force and distance sensors and can operate in air, liquids and vacuum. Although there are a vast range of commercial AFMs, none are specifically designed for tensile testing of nanofibres. Consequently, there are many methods for measuring mechanical properties by AFM. The most common approach is to move the cantilever perpendicular to the plane of the substrate, with the measured cantilever deflection providing normal force such as nanoindentation [42,43] or bending of a horizontally suspended nanofibre [44–49] to determine the material's Young's modulus or yield strength. Breaking strength and elongation at break are usually not measurable when using this geometry because the vertical range of motion for most AFM's is limited to a few micrometres.

A limited number of studies have used the horizontal motion of an AFM cantilever to measure the mechanical properties of nanofibres. The horizontal range of motion of most AFMs is at least an order of magnitude larger than the vertical range. When a fibre is mounted appropriately, it can be stretched to failure and provide the breaking strength and elongation at break in addition to the elastic and yield properties [50]. The two major difficulties arising with the mechanical testing of individual nanofibres via this lateral loading by AFM are: the accurate and convenient calibration of the spring constant for lateral deflection of the AFM cantilever; and the locating of individual fibres where they can be tested without slipping. The calibration of the lateral force of AFM cantilevers is still a matter of debate, despite lateral force measurements being produced with the AFM for almost 25 years [51,52]. Previously described methods for manipulation of individual fibres and fixing them at two points are both time consuming [53–56], and prone to add defects to the fibres.

Here, we describe a complete and simple approach to the preparation and tensile testing of individual electrospun nanofibres using an AFM. We introduce a method for fixing individual nanofibres across a gap that does not require additional handling of the fibres. We use the lateral movement of the AFM cantilever to enable tensile testing of the suspended fibres to high strains, and apply the lateral force calibration method proposed by Liu and co-workers [57] because of its geometric similarity to the fibre test. We further expand the calibration method to account for the inherent non-linearity of the AFM sensor and variable fibre/cantilever tip contact point. Errors in the determination of stress and strain are given. The developed method is applied to a range of electrospun polymers in both air and liquid to demonstrate the versatility of the technique. These studies reveal unique process and size dependent mechanical properties of electrospun polymers.

2. Experimental

2.1. Materials

Dimethylformamide (DMF), and tetrahydrofuran (THF), were obtained from AJAX Finechem. Buffer of pH 3 was prepared by mixing a ratio of 0.1 M citric acid (Sigma-Aldrich) and 0.2 M disodium hydrogen phosphate heptahydrate (Fluka) [58]. Poly(acrylic acid) (PAA) (M_w ~450,000 g/mol) was purchased from Polysciences, Polystyrene, (PS) (Austrex 103) was supplied by Polystyrene Australia. Poly(styrene-b-isobutylene-b-styrene) (SIBS) was a gift from Boston Scientific. All chemicals were used as received. Aqueous solutions were prepared using Milli-Q water (resistivity of 18.2 MΩ cm^{-1}).

2.2. Electrospinning nanofibres

A syringe with an internal diameter of 150 μm (Dispense Tips, Nordson EFD) and high voltage power supply (Gamma High Voltage ES-30) were used for electrospinning. The details of the electrospinning conditions for each polymer are included in Table 1.

The fibres were electrospun onto TEM grids with parallel bars (Gold, Gilder Grids) secured to glass slides with a small amount of nail polish (Sally Hanson) at opposite edges [59]. The space between the bars acts as a trench over which the fibres were suspended. During electrospinning, the TEM grids were positioned between parallel ground electrodes, which resulted in electrospun fibres stretching between the electrodes during deposition producing fibres that were aligned perpendicular to the bars of the TEM grid [60]. Some of the PAA nanofibres were chemically crosslinked by exposure to UV radiation under a nitrogen atmosphere (denoted as UVN_2) as described previously [61].

Table 1
Electrospinning parameters for the materials used.

Material	Voltage (kV)	Polymer concentration (%w/v)	Solvent	Syringe - collector distance (mm)	Atmosphere	Flow rate (ml/h)
PS	10	10	DMF	180	Air	0.15
SIBS	20	15	THF	100	Air	0.4
PAA	10	8	H_2O	180	N_2	0.2